

FORMATION OF QUINONES BY OXIDATIVE DEALKYLATION

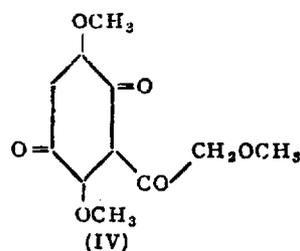
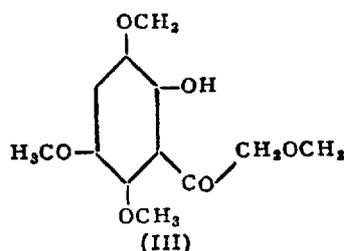
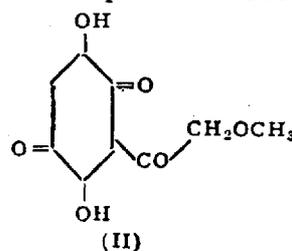
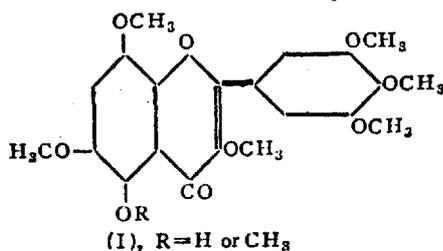
Part III. Alkali Fission of Gardenin

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IN the study of the constitution of flavones alkali fission is an important operation. The use of aqueous alkali or aqueous alcoholic alkali gives the acid product representing the side-phenyl nucleus fairly readily. It is not, however, satisfactory for the isolation of the ketonic product representing the fused benzene ring. Absolute alcoholic potash is much more useful. Even here only completely methylated or ethylated flavones undergo fission satisfactorily whereas partial ethers having free hydroxyl groups are resistant. Bose and Nath¹ reported that when gardenin, 5-hydroxy-3:6:8:3':4':5'-hexamethoxy-flavone (I, R = H), was boiled with 15 per cent. alcoholic potash, they obtained trimethyl gallic acid and a chocolate-coloured compound melting at 158–60° having only one methoxyl group and exhibiting quinone and acid properties. Subsequently Bose² drew attention to the similarity between this compound and 2:5-dihydroxy-quinones in general and pedicinin in particular and concluded that it should have the structure (II). Employing gardenin methyl ether (I, R = CH₃) for the alkali fission, Balakrishna and Seshadri³ showed that the fission went smoothly yielding a tetramethoxy-mono-hydroxy-ketone (III). By the action of nitric acid it underwent oxidative demethylation to form a neutral quinone-ketone (IV).



It was felt necessary to study the observation of Bose and Nath in greater detail since it constituted a case of oxidative demethylation by means of alcoholic alkali, the intermediate stage being probably ω :3:5-trimethoxy-2:6-dihydroxyacetophenone. Our present work confirms their observation. Further the constitution of the product is established as (II) by its preparation by the alkaline hydrolysis of the methoxy-quinone-ketone (IV). It should be noted here that all the nuclear methoxyl groups in ketone (III) can be removed through the stages (IV) and (II) because they are all in susceptible positions.⁴ Further alkali is required for the demethylation of (IV) in conformity with the behaviour of 1:2:4:5-tetramethoxybenzene derivatives.⁴

Expecting that the above described behaviour of gardenin with alcoholic alkali may be characteristic of partial methyl ethers of flavones with a free hydroxyl group in the 5-position a select number of analogous compounds having some of the features of gardenin have been studied. They are tetramethyl-ether of quercetin, pentamethyl ethers of myricetin, quercetagenin and gossypetin having a free hydroxyl in the 5-position and calycopterin having free hydroxyls in the 5- and 4'-positions. Surprisingly none of these underwent decomposition with alcoholic alkali under conditions when gardenin gave a good yield of the dihydroxy-quinone-ketone (II). Only their sparingly soluble potassium salts separated out and remained unaffected.

EXPERIMENTAL

ω -Methoxy-3:6-dihydroxy-2:5-quinone-acetophenone (II):

(i) *Hydrolysis of ω :3:6-trimethoxy-2:5-quinone-acetophenone (IV).*—The trimethoxy-quinone-acetophenone³ (0.8 g.) was just warmed with 40 per cent. aqueous potash (2 mols.) till a clear solution was obtained and cooled. The potassium salt separated out as a red solid. After allowing to stand for an hour it was filtered and washed with a small quantity of absolute alcohol. It was then dissolved in a few c.c. of water and the aqueous solution was acidified with dilute sulphuric acid. The brown solid that separated out, was extracted with ether and the ether solution concentrated. The product crystallised from alcohol as chocolate-coloured prisms melting at 159–60°. Yield, 0.3 g. (Found: C, 51.1; H, 4.0; OCH₃, 14.8; C₉H₈O₆ requires C, 50.9; H, 3.8 and OCH₃, 14.6%). An alcoholic solution of the substance, which was initially coloured orange, changed to dark brown on the addition of a drop of ferric chloride solution.

(ii) *Alkali fission of gardenin (I, R = H).*—Gardenin (2.0 g.) was treated with alcoholic potassium hydroxide (15%, 40 c.c.) and the mixture was

refluxed for six hours. The solution was left overnight in the refrigerator. The brown potassium salt that separated out was filtered and washed with a little absolute alcohol. It was dissolved in a small volume of water and worked up as described in the previous experiment. The final product was identical in all respects with the compound obtained above and the mixed melting point was undepressed.

The fission could also be effected with 8% alcoholic potash; but then the reaction was not quite complete in 6 hours and required longer boiling for completion.

SUMMARY

The observation of Bose and Nath regarding the fission of gardenin with alcoholic potash is confirmed. The formation of ω -methoxy-3:6-dihydroxy-2:5-quinone-acetophenone (II) in this reaction constitutes an example of oxidative demethylation by means of alcoholic potash. The same compound can be obtained from methyl gardenin through the stages (III) and (IV). Analogous partial methyl ethers of flavones with a free 5-hydroxyl are resistant to this treatment.

REFERENCES

1. Bose and Nath .. *J. I. C. S.*, 1938, 15, 139.
2. Bose .. *Ibid.*, 1945, 22, 233.
3. Balakrishna and Seshadri .. *Proc. Ind. Acad. Sci., A*, 1948, 27, 91.
4. Rao, Rao and Seshadri .. *Ibid.*, 1948, 27, 249.
Rao and Seshadri .. *Ibid.*, 1948, 27, 379.